

# Transverse acoustic nature of the excess of vibrational states in vitreous silica

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## Abstract

We present a numerical simulation study of the density-dependence ( $\rho=2.2\div 4.0$  g/cm<sup>3</sup>) of the high-energy collective dynamics in vitreous silica at mesoscopic wavevectors ( $Q=1\div 18$  nm<sup>-1</sup>). The density-dependence of the longitudinal and transverse current spectra provides evidence that the excess modes observed in the density of states of this and many other glasses, i.e. the Boson Peak, arises from the high- $Q$  limit of the quasi-*transverse* acoustic branch. This conclusion emerges from the comparison of the numerical results with the experimentally observed energy-shift and intensity variation of the Boson Peak with increasing density.

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Insulating disordered solids, when compared to their crystalline counterparts, exhibit some common peculiarities in their low-temperature thermal properties and low-energy spectroscopic features<sup>1,2</sup>, and in particular (i) a larger specific heat at temperatures up to  $\approx 1$  K, ascribed to tunneling processes<sup>3,4</sup>, (ii) a much smaller thermal conductivity, which also shows a plateau in the temperature range  $\approx 1 \div 10$  K<sup>1</sup>, (iii) a quasi-elastic light- and neutron-scattering intensity, and, most important, (iv) an excess of modes in the vibrational density of states, known as the Boson Peak (BP). An unambiguous understanding of the origin of these extra modes, and of their possible relation with other reported anomalies, is still missing, in spite of the extensive research effort primed by the pioneering work of Buchenau et al.<sup>5</sup> and continued by many authors<sup>6,7,8,9,10,11,12,13,14</sup>. No definite conclusion can yet be drawn as to the nature of the vibrational eigenvectors of the modes responsible for the BP: according to different authors, in fact, they are either spatially localized<sup>5,7</sup>, spatially delocalized and propagating<sup>6,9,13</sup>, spatially delocalized but diffusive in character<sup>15</sup>. Even more important, still we do not completely understand why should disorder accumulate vibrational eigenvalues in the same energy region, in such a broad variety of chemically and physically different materials. Some recent theoretical works have been devoted to this subject, and among them we recall (i) the work of Elliott and coworkers, who assigned the BP in glasses to the lowest-energy van Hove singularity of the corresponding crystal<sup>14,16</sup>; (ii) the work of Grigera et al., who interpreted the BP as the precursor of the dynamical instability expected in a disordered structure as function of density<sup>17</sup>; and (iii) the work of Götze and Mayr and that of Schilling et al., who obtained a spectral feature recalling the BP within a mode-coupling-like description of the high frequency dynamics of a model glass<sup>18,19</sup>.

In this Letter, we present a Molecular Dynamics (MD) study of the high-frequency dynamics in vitreous silica (v-SiO<sub>2</sub>) at different densities in the range  $\rho = 2.2 \div 4.0$  g/cm<sup>3</sup>. We demonstrate that the BP in vitreous silica arise from the high  $Q$  portion of the transverse acoustic branch. Our results quantitatively support and better specify i) the Elliott and coworkers' proposal<sup>14,16</sup> that the BP is connected to the van Hove singularity of crystalline quartz; and ii) the Buchenau finding<sup>5</sup> that the modes at the BP are local rotation of SiO<sub>2</sub> tetrahedra.

Experimentally, in SiO<sub>2</sub> at room pressure the BP appears as a broad peak in the plot of the Debye-normalized density of states  $g(E)/E^2$ , centered at  $\approx 5$  meV and having a width of  $\approx 5$  meV (Fig.1a). By increasing the sample density up to  $\rho = 4.0$  g/cm<sup>3</sup>, what is

observed<sup>20,21,22,23</sup> is a high-energy shift of the peak and its concomitant intensity decrease (Fig. 1b,c). In Fig. 1, the lines are experimental data, while symbols are the results of the present simulations (see below), and we would like to stress the excellent agreement between the two. It is important to realize that the excess of modes in the density of state itself  $g(E)$ , corresponding to the peak at  $\approx 5$  meV in  $g(E)/E^2$  of Fig. 1, is actually centered (at room pressure) around  $\approx 15$  meV, the shift being due to the  $1/E^2$  factor and to the very slow decay of the high frequency tail of the peak in Fig. 1. With respect to this point, it is important to underline that -in the high  $Q$  limit and in the one-excitation (one-phonon) approximation- the dynamic structure factor  $S(Q, E)$  becomes proportional to  $g(E)/E^2$ , and hence the longitudinal current spectrum  $C_L(Q, E) = E^2/Q^2 S(Q, E)$  becomes  $\propto g(E)$ . Therefore, the modes giving rise to the BP must be searched, in the current spectra, around 15 meV. This observation matches with the high  $Q$  panels of Fig. 2, where the computed currents (vide infra) show a broad bump at about this energy value.

The investigated system consists of 680 SiO<sub>2</sub> units ( $N=2040$  ions), enclosed in cubic boxes of different lengths (from  $L=3.1359$  nm, corresponding to  $\rho = 2.2$  g/cm<sup>3</sup> for the glass at room pressure, down to  $L=2.5693$  nm corresponding to a density of 4.0 g/cm<sup>3</sup>), with periodic boundary conditions. The ions interact through the BKS<sup>24</sup> two-body interaction potential; the long-range interaction was treated by the Ewald sum technique. As it has already been demonstrated, this system reproduce quantitatively the high frequency dynamics of vitreous silica<sup>9</sup>. The glass configuration at room pressure was obtained by standard MD methods for lowering the temperature down to 300 K starting from a well equilibrated liquid configuration at  $T=6000$  K, followed by a conjugate gradient geometrical minimization on the potential-energy hypersurface for an accurate location of the minimum. Such minimum configuration was taken as the starting point to generate a series of compressed systems. At each compression step, the box size was scaled by  $\approx 1.5\%$ , then the system was made to relax, and the new minimum configuration was searched by the conjugate gradient method. This procedure was repeated until the final density of 4.0 g/cm<sup>3</sup>, corresponding to a sample under an hydrostatic pressure of about 35 GPa<sup>25</sup>, was reached. A complete study of the structural and dynamical changes occurring during the compression will be reported in a forthcoming paper. We focus here on the changes in the high frequency dynamics that take place as the density is increased.

The vibrational dynamics in the minimum configurations was computed in the harmonic

approximation by diagonalizing the dynamical matrix, to obtain the eigenvalues ( $E_p$ ) and eigenvectors ( $e_p(i)$ ) of the  $p$ -th normal mode ( $p = 1 \div 3N$ ). From these quantities all vibrational characteristics can be derived. In particular, we have computed the density of states  $g(E)$  and the longitudinal and transverse currents spectra ( $C(Q, E)$ ) which, in the one-excitation approximation, are given by:

$$C_{\alpha\beta}^{\eta}(Q, E) = [K_B T / \sqrt{M_{\alpha} M_{\beta}}] \Sigma_p W_p^{\eta}(Q) \delta(E - E_p)$$

where  $\eta = L, T$ ,  $\alpha, \beta$  indicate Si and O, and  $W_p^{\eta}(Q)$  is the spatial power spectrum of the (longitudinal or transverse) component of the eigenvectors:

$$\begin{aligned} W_p^L(Q) &= |\Sigma_i (\hat{Q} \cdot \bar{e}_p(i)) \exp(i\bar{Q} \cdot \bar{R}_i)|^2 \\ W_p^T(Q) &= |\Sigma_i (\hat{Q} \times \bar{e}_p(i)) \exp(i\bar{Q} \cdot \bar{R}_i)|^2. \end{aligned} \quad (1)$$

Here  $\hat{Q} = \bar{Q}/|Q|$ .

The calculated  $g(E)/E^2$  are reported in Fig. 1 together with the corresponding experimental curves. The two sets of data compare favorably to each other, indicating the suitability of the employed potential model to follow the density dependence of the high frequency dynamics. In Fig. 2 we report longitudinal and transverse current spectra at selected  $Q$  values in the uncompressed sample ( $\rho = 2.2 \text{ g/cm}^3$ ). For  $Q$  values larger than about  $8 \text{ nm}^{-1}$ , both  $C^L(Q, E)$  and  $C^T(Q, E)$  show two distinct excitation maxima, a feature that becomes more and more evident at increasing  $Q$ . The excitation at higher energy disperses with  $Q$  and is observed at all  $Q$  values in the longitudinal current spectra, while it shows up as a weak shoulder in the transverse current spectra only at  $Q > 10 \text{ nm}^{-1}$ . In agreement with previous findings<sup>9,26,27</sup>, we assign this feature to the longitudinal sound-like branch. The behaviour of the low-energy excitation is in some sense complementary: it is always present in the transverse current spectra, while it appears in the longitudinal current spectra only at  $Q > 8 \text{ nm}^{-1}$ . At small  $Q$ , the low-energy peak disperses with a sound velocity of  $\approx 3800 \text{ m/s}$  (appropriate for the transverse sound mode), and becomes almost non-dispersing at  $Q > 8 \text{ nm}^{-1}$  (Fig. 3). We will call this low-energy feature -which is the main feature in the transverse current spectra- the transverse acoustic mode.

The presence of the signature of transverse dynamics in the *longitudinal* current spectra, and vice-versa, is only apparently surprising. Indeed, the polarization character of the modes (which is better and better defined at increasing wavelength, i. e. when the vibration sees

the medium as an elastic continuum) becomes ill defined at short wavelengths (*mixing* phenomenon). This is at the basis of the growth of peaks associated to the opposite polarization modes in the current spectra, and of the increased visibility of these peaks at increasing  $Q$  values. In Fig. 3 we report the computed dispersion curves of transverse excitations (open symbols) for samples of three densities ( $\rho = 2.2, 2.7, 4.0$  g/cm<sup>3</sup>), and of longitudinal excitations (crossed circles) of the uncompressed system<sup>29</sup>. In the same figure (full symbols), are also reported -at the available  $Q$  values, the experimental excitation energies (maxima of the current spectra) of the uncompressed SiO<sub>2</sub> glass, as measured by IXS and INS<sup>28,30</sup>. The agreement between MD and experimental data clearly indicates that the peaks observed in the INS experiment at  $Q$  larger than  $8\text{ nm}^{-1}$ , must be associated with the transverse dynamics, which appears in the measured (longitudinal) spectra due to the mixing.

In Fig. 3, we also observe a strong positive dispersion of the velocity of the (longitudinal) sound waves, which continue to propagate at energy well above the BP energy. This dispersion, observable also in MD simulations of Lennard-Jones glasses<sup>31</sup> and in previous v-SiO<sub>2</sub> calculations<sup>26</sup>, can be due to the interaction of the sound waves with a relaxation process<sup>31</sup> or with other modes. The investigation of the origin of the positive dispersion of  $v_L$ , and its possible interplay with the BP modes, is beyond the purpose of the present work.

For our present purposes, the first important result emerging from Fig. 3 is that the "transverse" branches (open symbols) in low- and intermediate-density samples, at large  $Q$ 's, flatten at high  $Q$ 's to an energy value which increases with increasing density ( $\approx 15$  meV at room condition and  $Q=15\text{ nm}^{-1}$ ). The density of vibrational states ( $g(E)$ ), associated with the branches which flatten, will have an excess of modes with respect to the Debye behaviour at these energies, reminiscent of the van Hove singularity of the corresponding crystal<sup>14</sup>. As mentioned, the corresponding peak in  $g(E)/E^2$ , will be red-shifted at lower energies ( $\approx 5$  meV at room condition). Therefore, we conclude that the Boson peak originates from the modes associated to the flat portion of the acoustic transverse dispersion curve.

This result is in agreement with the recent theoretical work of S. Taraskin et al., who associate the BP to the glassy counterpart of the lowest-energy van Hove singularity of the corresponding crystalline structure<sup>14</sup>. In this respect, it is worth noting that the transverse acoustic branch at  $Q$  larger than  $\approx 8\text{ nm}^{-1}$  is the glassy counterpart of a transverse optic phonon branch of  $\alpha$ -quartz (almost flat at  $\approx 4$  THz, i. e.  $\approx 16$  meV). This branch, in the extended Brillouin zone scheme which is more appropriate for disordered materials, is the

prosecution of the transverse acoustic branch<sup>32</sup>. According to Boysen et al.<sup>33</sup>, this branch is (close to the M-point) strongly temperature-dependent, and its softening is responsible for the  $\alpha$ - $\beta$  transition in quartz. More importantly, the atomic displacements induced by the lattice modes of this branch in quartz, as determined in<sup>32</sup>, are very similar to the frustrated localized rotation of  $\text{SiO}_4$  tetrahedra, that in vitreous silica -according to Buchenau et al.<sup>5</sup>- are the modes contributing to the BP.

The assignment of the BP to the flattening of the transverse acoustic branch is strengthened by the behaviour of the high-energy transverse dynamics upon densification. Spectra similar to those of Fig. 2, but for the sample at the highest studied density ( $\rho=4.0 \text{ g/cm}^3$ ), are reported in Fig. 4, while the corresponding dispersion curves are reported in Fig. 3. One can observe that (i) the two current spectra are now "pure", and no evidence of wrong-polarized modes is present; (ii) the positive dispersion of the L-branch is absent; and, more importantly, (iii) the T-branch no longer shows a flattening. This latter observation, together with the experimental and numerical finding that the BP intensity strongly decreases on increasing density<sup>21,22,23</sup> (as evident in Fig. 1), gives a decisive support to the finding that the BP is produced by the flattening of the quasi-TA branch.

In conclusion, by comparing the spectra of the longitudinal and transverse current, and by studying their density dependence, we have shown that the BP in v- $\text{SiO}_2$  is to be ascribed to the quasi-transverse acoustic modes, whose dispersion relation becomes  $Q$ -independent at high  $Q$ , and consequently, gives rise to an excess of modes with respect to the Debye behaviour. The whole picture presented here reconciles different previous studies on the origin of the BP: i) the high  $Q$  part of the transverse acoustic branch in vitreous silica -which gives rise to the BP- is the counterpart of a low lying transverse optic branch in  $\alpha$ -quartz<sup>32</sup>; ii) according to Boysen et al.<sup>33</sup> the softening of this branch at the M-point give rise to the  $\alpha$ -to- $\beta$  transition; iii) in agreement with i) and ii), according to Taraskin et al.<sup>14,16</sup>, the BP arises from the softening of the lowest-energy van Hove singularity of the corresponding crystals; iv) according to Dorner and coworkers the eigenvectors of this branch in quartz correspond to rotation of  $\text{SiO}_4$  tetrahedra; v) finally, in agreement with i) and iv), according to Buchenau et al.<sup>5</sup> the modes contributing to the BP are localized rotation of  $\text{SiO}_4$  tetrahedra.

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## FIGURE CAPTIONS

FIG. 1: Normalized density of states  $g(E)/E^2$  of vitreous silica at three different densities  $\rho$ : (a) 2.2 g/cm<sup>3</sup> (full line and circles); (b) 2.7 g/cm<sup>3</sup> (dashed line and squares); (c) 4.0 g/cm<sup>3</sup> (triangles). Lines are experimental data from Ref.<sup>22</sup>, symbols are the results of the present simulation.

FIG. 2: Selected examples of longitudinal (full lines) and transverse (dashed lines) current spectra at the indicated  $Q$ -values in nm<sup>-1</sup>, for the sample at  $\rho=2.2$  g/cm<sup>3</sup>.

FIG. 3: Dispersion relation of the main peaks appearing in the current spectra. Crossed circles are the maxima of the longitudinal current at  $\rho=2.2$  g/cm<sup>3</sup> (the line is a guide for the eyes). The open symbols refer to the maxima of the transverse current at  $\rho=4.0$  g/cm<sup>3</sup> (down-triangles),  $\rho=2.7$  g/cm<sup>3</sup> (squares),  $\rho=2.2$  g/cm<sup>3</sup> (up-triangles). Full symbols are INS (squares) and IXS (circles and diamonds) experimental data for  $\rho=2.2$  g/cm<sup>3</sup> taken from Ref.s <sup>6,28,30</sup>.

FIG. 4: Selected examples of longitudinal (full lines) and transverse (dashed lines) current spectra at the indicated  $Q$ -values (in nm<sup>-1</sup>) for the highest density sample ( $\rho=4.0$  g/cm<sup>3</sup>).

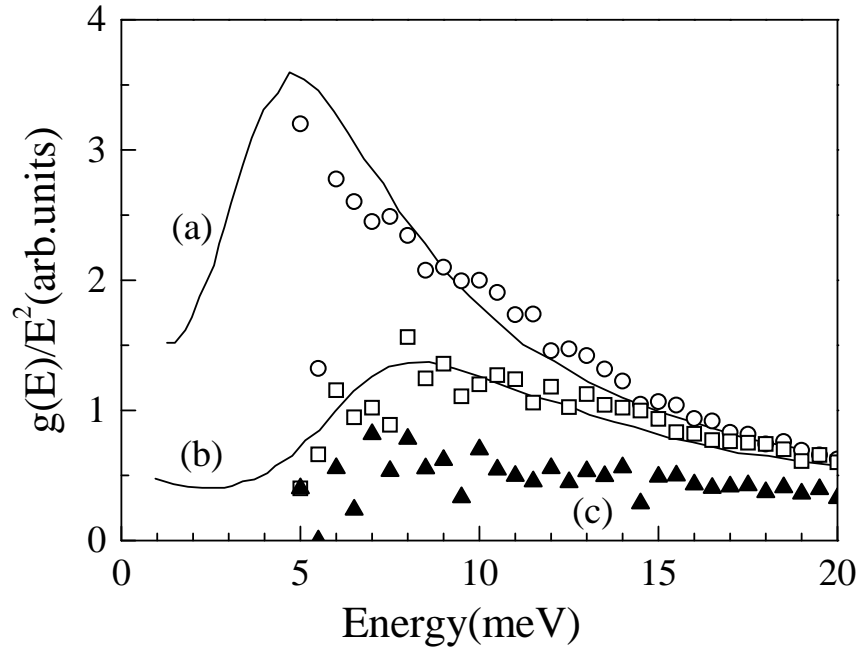


Figure 1. Pilla et al.

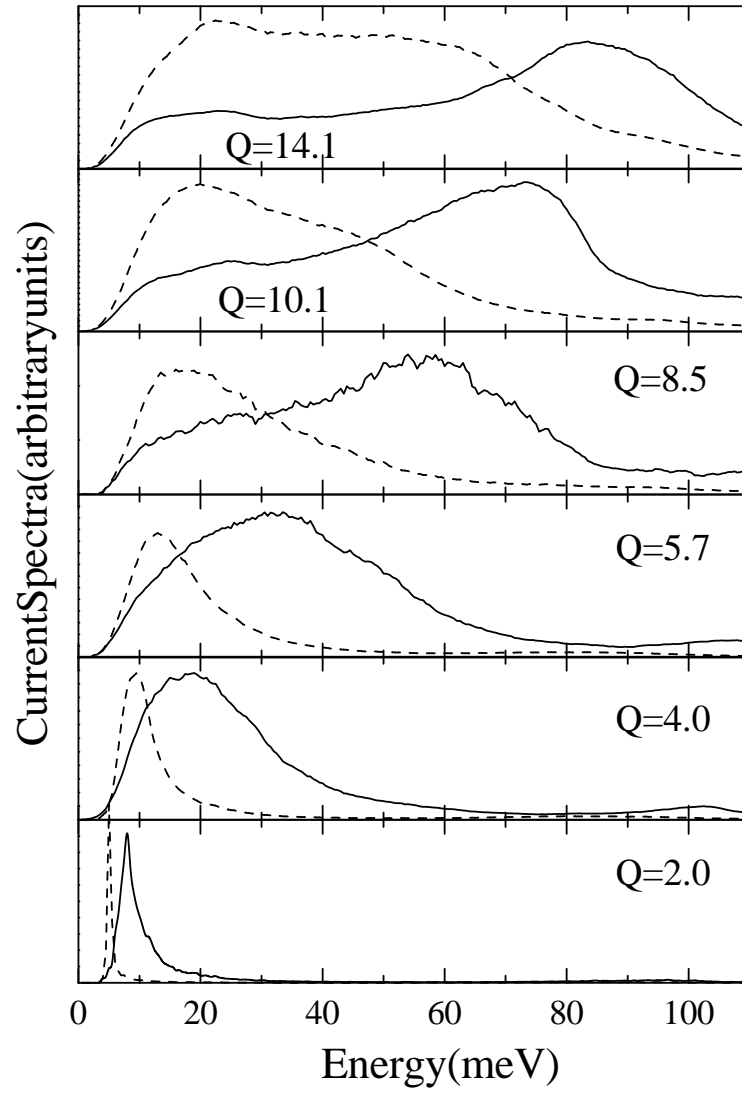


Figure 2. Pilla et al.

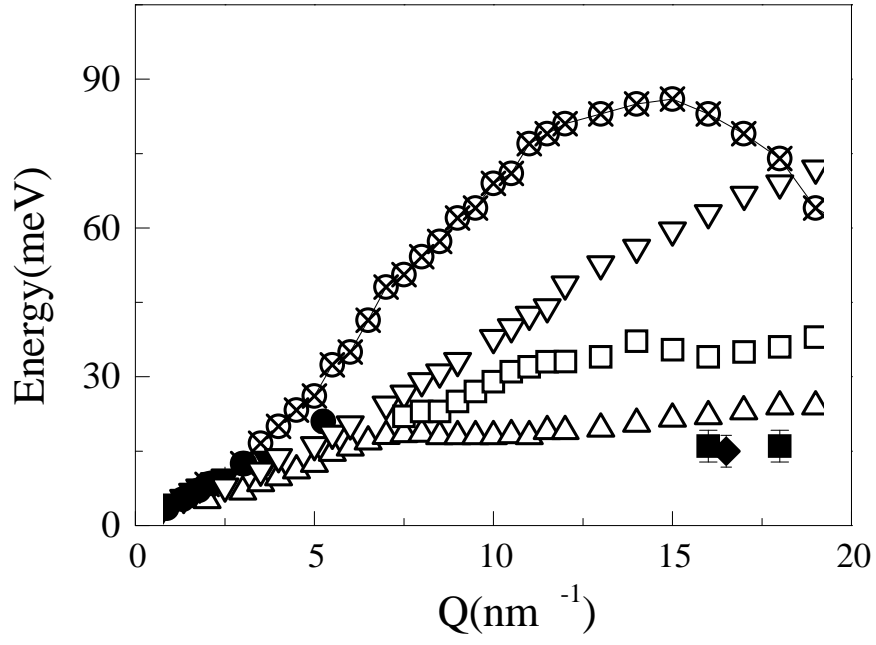


Figure 3. Pilla et al.

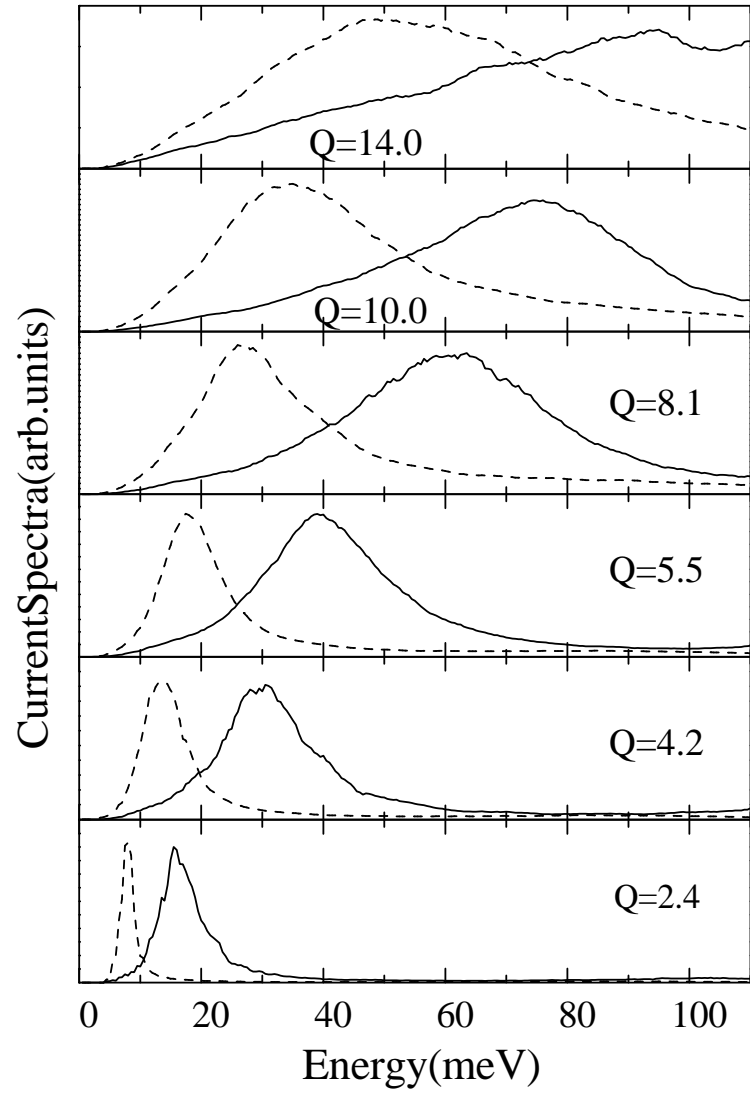


Figure 4. Pilla et al.